

## SPECIFICATION

## Powdered Molding Powder for Continuous Casting of Steel

## Technical Field

0001 The present invention relates to a powdered molding powder for continuous casting of steel that is provided onto a molten steel surface in a mold during continuous casting of steel.

## Related Art

0002 In the continuous casting of steel, a molding powder is added onto a molten steel surface in the mold, is melted and slagged by heat derived from the molten steel to form a molten slag layer, and progressively flows into a gap between the mold and a cast slab, to be consumed. Examples of primary functions of the molding powder during this time include: (1) lubrication between the mold and the cast slab; (2) absorption of inclusions which float from the molten steel; (3) prevention of reoxidation of the molten steel, and heat insulation thereof; and (4) control of the rate of heat transfer from the solidifying shell to the mold.

0003 A chemical composition of the molding powder usually contains  $\text{SiO}_2$  and  $\text{CaO}$  as a main (base) component, and is further constituted from elements such as  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{BaO}$ ,  $\text{SrO}$ ,  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{F}$ ,  $\text{MnO}$ ,  $\text{B}_2\text{O}_3$ , carbonaceous raw material and the like. Raw materials comprise a base raw material, silica raw material, flux raw material, carbonaceous raw material and the like. For example, portland cement, synthesized calcium silicate, wollastnite, blast furnace slag, yellow phosphorous slag, dicalcium silicate ( $2\text{CaO} \cdot \text{SiO}_2$ ) and the like may be used as the main raw material. Also, the silica raw material is added in order to adjust the powder properties such as basicity ( $\text{CaO}/\text{SiO}_2$  mass ratio), bulk density and the like, and for example,

glass, silica rock, diatomaceous earth and the like may be illustrated. The flux raw material functions as an adjusting agent for melting properties such as softening point, viscosity and the like and for example, fluorides such as fluorite, cryolite, borax, sodium fluoride, magnesium fluoride, etc., carbonates such as sodium carbonate, lithium carbonate, manganese carbonate, barium carbonate, etc., and the like may be employed. Further, the carbonaceous raw material functions as a melting speed adjusting agent and exothermic agent, and carbon black, coke, graphite, acid-treated graphite and the like may be used.

0004 Also, the shape of the molding powder for continuous casting of steel is classified to powdered or granular form. An advantage of the granular molding powder is the low dusting amount. On the other hand, in order to improve operating stability of the continuous casting and quality of the obtained steel, a powdered molding powder is suitable, since the powdered molding powder has superior heat retaining properties for molten steel, and melting properties.

0005 Conventionally, in order to prevent sintering and to adjust the melting speed of the powdered molding powder, not less than 1 percent by mass (weight) of carbon black is added to the molding powder. However, as described hereinafter, the addition of carbon black is not preferable with regard to the operating conditions and work environment. Therefore, a molding powder wherein the amount of carbon black added is remarkably lowered, has been developed. For example, Patent document 1 discloses a colored powder for continuous casting characterized in that not more than 0.7 percent by mass (weight) of carbon black and not less than 0.5 percent by mass (weight) of a pigment other than carbon black are compounded to a base raw material, and hollow and spherical form powder particles are possible (claim 1); and a colored powder for continuous casting characterized in that not more than 0.7 percent by mass (weight) of carbon

black and not less than 0.5 percent by mass (weight) of a pigment other than carbon black are compounded to a base raw material and the sum of sodium fluoride (NaF), cryolite ( $3\text{NaF} \cdot \text{AlF}_3$ ) and soda ash ( $\text{Na}_2\text{CO}_3$ ) in the base raw material is not more than 5 percent by mass (claim 2).

0006 Further, Patent document 2 discloses a powdered flux for casting iron metal characterized in that said flux comprises (1) a sintered or molten composition containing a fire resistant metal oxide and a solvent; and (2) a cellulosic material.

0007 Further, Patent document 3 discloses a molding powder for continuous casting of steel characterized in that from 0.5 to 5 percent by weight (percent by mass) of carbonaceous powder of under 100 mesh and from 0.1 to 4 percent by weight (percent by mass) of organic fibrous material of under 100 mesh as a melting speed adjusting agent are compounded to a base material for the molding powder that is constituted mainly by metal oxides and contains one or more components selected from a group consisting of alkali metal or alkali-earth metal fluorides, alkali metal oxides or carbonates.

0008 Also, Non-Patent document 1 reports a molding powder wherein cellulose is added to the powder thereby speeding melting speed in order to make the thickness of a molten layer in a mold uniform.

0009 Patent document 1: Japanese Patent Laid-Open No. 8-25007;

Claims

Patent document 2: Japanese Patent Laid-Open No. 56-89372;

Claims

Patent document 3: Japanese Patent Laid-Open No. 59-27759;

Claims

Non-Patent document 1: Nippon Steel Technical Report, Vol. 377 (2002), pp55-58 [Development of Technology to Improve Surface Layer

Quality of Continuous Cast 304  
Austenitic Stainless Steel Ingots]

Disclosure of the Invention

Problems to be Solved by the Invention

0010 In conventional powdered molding powders, in order to control melting speeds and to maintain melting properties, not less than 1 percent by mass (weight) of carbon black is usually added. The reasons why carbon black has remarkable effects in preventing sintering and in adjusting melting speed are as follows. Surfaces of all raw material particles that constitute the powdered molding powder are completely covered by carbon black, since carbon black has strongly adhesive properties and dispersibility. Also, since carbon black has wetting resistance to slag, from the time the powdered molding powder is heated until it reaches a softening and melting temperature, fusion between raw material particles can be inhibited and the sintering and melting thereof can be delayed by carbon black which prevents direct contact between the raw material particles.

0011 Where there is excess carbon black in present the powdered molding powder, when the molten metal has a smooth surface, the molding powder melts upward smoothly progressively from the bottom, but when the molten metal has a disturbed surface such as when there is a lot of gas floating up from the molten metal, the unmelted molding powder turns red from heat and flows. Such a phenomenon is referred to as red heat. The red heat phenomenon takes place because carbon black excessively covers surfaces of raw material particles of the molding powder, and thus, fusion between the raw material particles does not occur at all even when the raw material particles are heated to a softening and melting temperature, and the raw material particles are liable to flow. When the red heat phenomenon takes place, flowing molding powder serves as a heating medium to enhance heat

dissipation from the molten metal surface and to cool the molten metal surface in which heat insulation is essentially important, thereby developing problems of deteriorated quality of the cast slab and causing breakout in some cases. Further, when the red heat phenomenon takes place, the molding powder is also cooled to delay the melting and it becomes difficult to maintain an appropriate thickness of the molten layer. Then, supply of slag flowing between the mold and the solidifying shell stops, so that there is also the problem of breakout occurring easily. Thus, an excess amount of carbon black drastically changes melting properties due to the active state of the molten metal surface, resulting in disadvantages such as the occurrence of product defects and deterioration of operating stability.

0012 On the other hand, in the presence of a small amount of carbon black in the molding powder, the raw material particles are in direct contact with each other and are fused from a relatively low temperature equal to or lower than the melting point, thereby developing problems of causing sintering easily and too rapid melting. The molding powder is sintered to form a lump of a sintered product referred to as a slag bear on a periphery of the mold, to inhibit flow of a powder slag between the mold and the solidifying shell, and to cause failure in lubrication of the solidifying shell, thereby causing breakout in some cases. Too rapid melting of the molding powder disturbs a balance in the flow rate of the molten powder slag between the mold and the solidifying shell, thereby causing a problem of forming too thick a molten slag layer. Too thick a molten slag layer adversely affects the operation stability and product quality to a great extent due to deterioration of melting properties, deterioration of heat insulation properties, increase in fluctuation of a molding powder composition, and the like.

0013 As described above, the amount of carbon black added remarkably depends on the melting properties of the powdered molding powder, and at

the present time, it is difficult to improve adaptability to changes in operating conditions in a conventional powdered molding powder.

0014 Further, the melting properties of the powdered molding powder vary remarkably according to the mixing conditions at the time of production even if the amount of carbon black added is the same. That is, since the carbon black does not be uniformly coat to the surface of raw material particles, if the mixing conditions are bad, nonuniform melting can be generated and the melting speed may be faster than the expected speed. On the other hand, if the mixing conditions are too good, it becomes easy for a red heat phenomenon to occur. As described above, in the powdered molding powder with added carbon black, there is a problem in that setting production conditions becomes very difficult.

0015 Nevertheless, usually, more than 1.0 percent by mass (weight) of carbon black is added to most all conventional powdered molding powders in order to control the melting speed and maintain the melting properties, accordingly, the color of the powdered molding powder is naturally black. The soiling from dusting by black color powdered molding powder is readily apparent, and when the powder adheres to equipment, clothes, skin and the like, there is a problem in that the soil cannot be easily removed. Also, since most all powdered molding powders are black, there is no difference of color for each product (quality), accordingly, distinction of products (qualities) cannot be carried out by appearance alone. Therefore, if an error of addition of powdered molding powder is caused by an operator, the operator cannot recognize the error and operational trouble may occur. However, it is felt that such molding powder adding errors may become more difficult to occur, if the color for each product (quality) differs with each other.

0016 Next, the colored powder for continuous casting described in Patent document 1 prevents degradation of the melting property by being limited

form to hollow granules, and limiting the total amount of sodium fluoride, cryolite and sodium carbonate that are low melting point raw materials, if the molding powder is in powdered form. However, in Patent document 1, since carbon black is only compounded at an amount of not more than 0.7 percent by mass (weight), so it is difficult to control slagging and melting speed just by limiting the total amount of sodium fluoride, cryolite and sodium carbonate, and further the degradation of melting properties is difficult to prevent, so said colored powder is imperfect.

0017 Further, Patent document 2 discloses the addition of a cellulosic material to powdered flux (mold powder) for casting of iron metal in order to inhibit the formation of clinker. However, since no elementary carbon is contained, combustion of the cellulose material occurs, and oxidation of the carbide that is formed by the combustion is too fast. There is therefore a problem that the generation of sintering material becomes facilitated.

0018 Also, even though Patent document 3 discloses a molding powder to which is added carbonaceous powder and organic fibrous material, an object of the combination of carbonaceous powder with organic fibrous material is to maintain a melted slag layer, thereby preventing carburizing. Further, there is no concrete description in Patent document 3 concerning the compounding amount of carbon black and in the working examples, 2.0 percent by mass (weight) of carbon black was added to the powdered molding powder. However, red phenomena can easily occur in this molding powder and the color of the mold powder is black. Further, without carbon black, this is only granular molding powder.

0019 Also, in the molding powder used in Non-Patent document 1, even if cellulose is employed, it is impossible for the melting speed to be accelerated.

0020 Therefore, an object of the present invention is to provide a powdered molding powder for continuous casting of steel which has

melting properties allowing: maintenance of an appropriate melting rate without formation of a slag bear or a sintered product; prevention of a red heat phenomenon even when a molten steel surface is active; prevention of contamination due to dust formation by having a color tone besides black; and easy distinction of products by being colored any color except black.

#### Means for Solving the Problem

0021 Accordingly, the present invention provides a powdered molding powder for continuous casting of steel characterized in that the powdered molding powder contains not more than 0.5 percent by mass (weight) (including zero) of carbon black, from 0.5 to 20 percent by mass (weight) of carbon powders other than carbon black and from 0.1 to 7.0 percent by mass (weight) of carbohydrate powder as a carbonaceous raw material.

0022 Also, the powdered molding powder for continuous casting of steel according to the present invention is characterized in that the powder contains from 0.1 to 8.0 percent of mass (weight) of acid-treated graphite as a part or all of the carbon powders other than carbon black.

0023 Further, the powdered molding powder for continuous casting of steel according to the present invention is characterized in that the powder contains from 0.3 to 7.0 percent by mass of pigment.

#### Effect of the Invention

0024 The powdered molding powder for continuous casting of steel according to the present invention exerts the effects of: contamination due to dust formation being inconspicuous to improve the operating environment since the molding powder has a color tone other than black; and smooth melting without occurrence of a red heat phenomenon even when the molten steel surface is active in terms of melting.



### Best Mode for Carrying Out the Invention

0025 When the amount of carbon black added is reduced to eliminate problems due to excess carbon black in the molding powder for continuous casting of steel, a substance for preventing fusion between molding powder particles may be added after the molding powder is exposed to heat. The present inventors have conducted various studies and have found that carbohydrates can be used as a raw material alternative to carbon black. Carbohydrate powder that is dispersed in per se the molding powder for continuous casting disperses among the raw material particles of the molding powder to prevent fusion therebetween, and is carbonized by heat in use to coat the surfaces of the raw material particles of the molding powder, thereby preventing fusion between the raw material particles of the molding powder.

0026 However, if in the absence of carbon powder, carbohydrate powder is used alone, it is easy for the carbohydrate powder to combust completely, making it difficult for carbide to form, so that the fusion between raw material particles of the molding powder together cannot be prevented and the melting speed of the powdered molding powder cannot be delayed. Hence, by adding carbohydrate powder and carbon powder simultaneously, carbohydrate powder is subjected to incomplete combustion to form carbide and coat the raw material particles of the mold powder, so that sintering can be prevented and the melting speed can be controlled. Further, even among carbon powders, the addition of acid-treated graphite is preferable, since when this graphite is heated, the graphite itself expands to prevent the fusion of raw material particles to each other in the mold powder, thereby increasing the sintering preventive effects.

0027 In the powdered molding powder for continuous casting of steel according to the present invention, carbohydrate powder that is added as raw material alternative to carbon black is not limited in particular as long

as it contains carbohydrate as a main component, and powders that are obtained by grinding cereals or root crops such as rice, wheat, soybean, corn, corm and the like; manufactured goods such as starch powder, cellulose and the like that are produced from cereals or root crops; waste paper powder and wood chip grinding powder may be used. Among carbohydrate powders, it is preferable that wheat powder, dogtooth violet starch powder, starch powder and carboxymethylcellulose (CMC) are easily available and have good particle size.

0028 The compounding amount of the carbohydrate powder ranges from 0.1 to 7.0 percent by mass (weight), preferably from 0.3 to 4.0 percent by mass (weight). The carbohydrate powder functions to disperse between the raw material particles of the molding powder, thereby preventing fusion of said particles as well as to carbonize when the carbohydrate powder is heated during the operation, to coat the particle surface of the raw material of the molding powder, thereby preventing fusion between the raw material particles of the molding powder. Accordingly, if the compounding amount of the carbohydrate powder is less than 0.1 percent by mass (weight), the melting speed of the molding powder for continuous casting of steel cannot be controlled and sintering can not be prevented, which is not preferable. Further, if this amount is more than 7 percent by mass (weight), although the melting property is good, it is not preferable as the melting is too late. Smaller particle size carbohydrate powder is preferable as it tends to easily disperse, so that the coating of the carbohydrate powder to the raw material particles for the molding powder is remarkably high and the fusion together of the raw material particles for the molding powder can be prevented. That is, the particle size of the carbohydrate powder ranges preferably from under 100 mesh, more preferably under 150 mesh.

0029 In the powdered molding powder for continuous casting of steel, the amount of carbon black added is preferably not more than 0.5 percent by

mass (weight), more preferably not more than 0.3 percent by mass (weight), much more preferably 0.1 percent by mass (weight) with no carbon black being most preferable. If a large amount of carbon black is added, it is easy for the red heat phenomenon to occur when the molten steel surface in the mold is active, so it is not preferable. Also, if carbon black and carbohydrate powder are added simultaneously, irregular melting speeds in the molding powder are generated locally, accordingly, deterioration of the melting properties can be recognized. Since the dispersibility of carbohydrate powder is degraded by carbon black, it is preferably that smaller amounts of carbon black are added. Further, when the amount of carbon black added is great, the color of the molding powder becomes black, which is not preferable. It is not preferable that the amount of carbon black added be more than 0.5 percent by mass (weight), because it causes red heat phenomenon, the melting properties degrade and the color tone becomes black.

0030 To the powdered molding powder for continuous casting of steel according to the present invention, carbon powders other than carbon black are added. For example, one or more of coke, graphite, acid-treated graphite and the like can be used as the carbon powders other than carbon black. The total amount of carbon powders other than carbon black added ranges from 0.5 to 20 percent by mass (weight), preferably from 1.0 to 10 percent by mass (weight). If the total amount of carbon powders other than carbon black added is less than 0.5 percent by mass (weight), since combustion speed of the carbohydrate is too fast, it is not preferable as the melting speed of the molding powder is too fast and sintering tends to be caused easily. Also, if the amount of carbon powders other than carbon black added is more than 20 percent by mass (weight), it is not preferable as the melting speed of the powdered molding powder is too slow. Further, it is not preferable as the color tone of the obtained powdered molding powder is

black.

0031 In the powdered molding powder for continuous casting of steel according to the present invention, the acid-treated graphite can be preferably used as a part or all of the carbon powders other than carbon black added. The amount of acid-treated graphite added ranges preferably from 0.1 to 8.0 percent by mass (weight), more preferably from 0.3 to 3.0 percent by mass (weight). If the amount of acid-treated graphite is less than 0.1 percent by mass (weight), the sintering inhibiting effect of the powdered molding powder is small and no adding effect is found. Also, if the amount of acid-treated graphite is more than 8.0 percent by mass (weight), it is not preferable as the dusting from expansion is remarkably increased. Further, in order to obtain a certain amount of expansion, an exorbitantly small particle size of acid-treated graphite is not preferable, so acid-treated graphite having from 325 to 10 mesh particle size range for example, may be preferable. Also, since coke or graphite with a smaller particle size has greater adding effects, those having under 100 mesh, for example, preferably under 150 mesh of particle size may be preferable.

0032 Bulk density of the powdered molding powder for continuous casting of steel according to the present invention is less than 1.0, preferably less than 0.9. If the bulk density of the powdered molding powder is greater than 1.0, it is not preferable as good melting properties cannot be maintained, since raw material particles easily contact each other.

0033 In order to obtain a desired color tone, a pigment may suitably be added to the powdered molding powder for continuous casting of steel according to the present invention. A compounding amount of the pigment is not less than 0.3 percent by mass (weight). If the amount is less than 0.3 percent by mass (weight), it is not preferable as there is no effect from adding the pigment. Also, the upper limit of said amount differs depending on the kind of pigment used, but it is approximately 7 percent by mass

(weight). If this amount is greater than 7 percent by mass (weight), it is not preferable as other components that constitute the powdered molding powder for continuous casting of steel may be affected. By suitably selecting the pigment, the powdered molding powder for continuous casting of steel can be pigmented to a desired color tone such as red, blue, yellow, green, purple and the like. Also, an organic or inorganic pigment may be used, but an organic pigment having a strong tinting strength in small amounts is more preferable. Further, for example, red iron oxide, umber, yellow ocher and the like may be illustrated as inorganic pigments, and alizarin lake, phthalocyanine green, phthalocyanine blue, greenish yellow and the like may be illustrated as organic pigments.

0034 Further, raw materials other than those described above that constitute the powdered molding powder for continuous casting of steel according to the present invention are not particularly limited, and can be constituted from conventional main raw materials, silica raw materials, flux raw materials and the like. For example, portland cement, synthesized calcium silicate, wollastnite, blast furnace slag, yellow phosphorous slag, dicalcium silicate ( $2\text{CaO} \cdot \text{SiO}_2$ ) and the like may be illustrated as the main raw material. Also, the silica raw material is added in order to adjust the powder properties such as basicity ( $\text{CaO}/\text{SiO}_2$  mass ratio), bulk density and the like. The flux raw material functions as an adjusting agent for the melting properties such as softening point, viscosity and the like and for example, fluorides such as fluorite, cryolite, borax, magnesium fluoride, etc., carbonates such as sodium carbonate, lithium carbonate, manganese carbonate, barium carbonate, etc., and the like can be employed. Further, the amount of these raw materials added is not particularly limited, and ranges from 98 to 40 percent by mass (weight), preferably from 80 to 50 percent by mass (weight) of the main raw material, from 0 to 40 percent by mass (weight), preferably 3 to 20 percent by mass (weight) of silica raw

material and from 0 to 40 percent by mass (weight), preferably from 3 to 30 percent by mass (weight) of the flux raw material, for example.

0035 Also, the basicity [ $\text{CaO}/\text{SiO}_2$  mass (weight) ratio] of the powdered molding powder for continuous casting of steel according to the present invention is not particularly limited, the present invention can be adapted to a powdered molding powder having from 0.3 to 2.5 basicity.

### Examples

0036 Hereinafter, the molding powder for continuous casting of steel according to the present invention will be further described based on examples. Powdered molding powder for continuous casting as inventive products and as comparative products shown in Table 1 were prepared by using as a base a molding powder for continuous casting having properties of a  $\text{CaO}/\text{SiO}_2$  mass ratio of 0.88 and molten slag viscosity of 4 poise at  $1300^\circ\text{C}$ . A base raw material other than carbohydrate powder, carbon and pigments included: 69 percent by mass (weight) of synthetic calcium silicate as a main raw material; 9 percent by mass (weight) of a silica raw material; and 22 percent by mass (weight) in total of sodium fluoride, calcium fluoride, sodium carbonate, lithium carbonate, alumina and magnesia as flux raw material. Bulk specific gravity of the obtained molding powder fell within a range of 0.71 to 0.73.

An actual casting test was carried out using the obtained powdered molding powder. Casting conditions were: low carbon steel; a mold size of  $210\text{mm} \times 1,500\text{mm}$ ; and a casting speed of  $1.4\text{m/minute}$ . Table 1 shows the results of the casting test.

Further, the melting properties were evaluated comprehensively from visual observation and bead formation. The melting speed was determined by measuring the thickness of the molten layer to evaluate whether a stable constant value was secured. The operating environment

was evaluated from a level of contamination due to adhered molding powder. The product quality was evaluated from cracks in the obtained cast slab and inclusions.

Table 1 shows the obtained results.

Table 1

		Inventive Product											Comp. Product	
		1	2	3	4	5	6	7	8	9	10	11	1	2
Compounding	Carbohydrates	wheat flour	2.3											
	Ratio	dogtooth violet starch	2.3			1.0	0.5	3.5	4.0	2.0	2.0	2.0		
	(mass %)	CMC		1.5										
		cellulose			2.3	2.0								
Carbons	carbon black							0.3						0.8
	coke	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5		
	graphite	1.0	1.0	1.0	1.0	1.0	0.5		1.0	1.0	1.0	1.0		1.5
	acid-treated graphite	1.5	1.5	1.5	1.5	1.5	1.5	0.5	1.5	1.5	1.5	1.5		1.5
Pigments	phthalocyanine green									0.5				
	greenish yellow										2.0			
	red iron oxide											3.0		
Shape		powder	powder	powder	powder	powder	powder	powder	powder	powder	powder	powder	powder	powder
Color		white	white	white	white	white	gray	gray	white	green	yellow	red	white	black
Results used	Melting property	O	O	O	O	O	O	Δ	O	O	O	O	O	O
	Melting speed	O	O	O	O	O	Δ	Δ	Δ	O	O	O	×	O
	Operating environment	O	O	O	O	O	O	O	O	O	O	O	O	×
	Product quality	O	O	O	O	O	Δ	O	O	O	O	Δ	×	O



0038 Also, in Table 1, carbohydrate, coke and graphite powders having under 150 mesh of particle size were used. Further, acid-treated graphite having under 65 mesh of particle size was used.